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Technical Report No. 8

CRAZE INITIATION CRITERION IN GLASSY  
POLYMERS UNDER HIGH PRESSURE

by

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# ABSTRACT

The initiation of crazes in glassy polymers is accounted for by a single criterion according to which crazing occurs when the maximum stress at the tip of a flaw ( $\sigma_{\max}$ ) reaches a critical value. This criterion can explain the initiation of crazes in polymethylmethacrylate and polystyrene tested in tension under superposed hydrostatic pressure. A single value of  $\sigma_{\max}$  for each of the two polymers has been calculated and found to be independent of the applied hydrostatic pressure whether or not the polymer was exposed to the pressure-transmitting fluid. Our analysis predicts that relatively small stress-concentrations suffice for craze initiation even under remote compressive stress states (negative first stress invariant). The predicted stress concentrations are in reasonable agreement with experimentally determined values.

## 1. Introduction

Observations of crazing in glassy polymers subjected to non-dilational stress fields<sup>1-4</sup> can not be explained using current theories of craze initiation,<sup>5-8</sup> which require a positive first stress invariant. Discrepancies between the experimental data and the theories were incorrectly thought to be due to procedural errors in the experimental arrangement.<sup>1</sup> However, if the critical role played by surface flaws is considered rather than the overall remote stress applied during deformation, a criterion for craze initiation which does not necessarily depend on the first stress invariant can be described. Guided by this subtle, yet fundamental point, we shall attempt to furnish a better understanding for the stress field required for craze initiation, whether the polymer is exposed or protected from an environmental fluid considered to be inert.

In a recent publication<sup>9</sup>, Gent hypothesized that high elastic concentrations exist at the tips of surface flaws which produce large negative pressures thus causing devitrification of the glassy polymer. The devitrified material then cavitates under such pressure, leading to craze formation. By assuming extremely high stress concentration factors, this theory qualitatively agrees with the observations of crazing in tension under high hydrostatic pressure reported by Baer and coworkers<sup>1</sup>. This theory, however, did not account for the observed pressure coefficient of the craze initiation stress. In a more recent publication,<sup>10</sup> this anomaly was attributed to an "effective tip radius increase" of the started flaw, an assumption which cannot be substantiated by current electron microscopy studies. Additionally, none of the theories of craze formation have considered the problem arising when the polymer is in contact with the pressure transmitting fluid.

The purpose of this paper is to suggest and present experimental evidence for a new craze initiation criterion for glassy polymers based on more accurate calculations of the maximum stress at the tip of a flaw. Both cases are considered, i.e., polymer protected from and exposed to fluid environment. The craze behavior of polymethylmethacrylate and polystyrene under high hydrostatic pressure is examined in light of the proposed criterion.

## 2. Theoretical Treatment

Fundamental considerations of the well established craze microstructure, its orientation perpendicular to the direction of maximum tensile stress, and the critical role played by surface flaws suggest that a viable craze initiation criterion has to be based on maximum tensile stress at the tip of a flaw ( $\sigma_{\max}$ ). A critical state occurs when  $\sigma_{\max}$  becomes large enough to cause the flaw tip, by whatever means, to grow into a craze.

A generally accepted structural feature of solid glassy polymers is the existence of microheterogeneities (microvoids) whose volume depends on the chemical structure of the polymer as well as on its thermomechanical history. For the purpose of illustration, figure 1 shows the geometry we have assumed for a surface heterogeneity (flaw). It will be shown later in the discussion that this geometry provides theoretical results which are in good agreement with the experimental data. The stress-concentration associated with such a flaw or hole depends on whether the hole is empty or filled with the pressure-transmitting liquid when the polymer is subjected to a remote tensile stress ( $\sigma$ ) concurrently with a hydrostatic pressure ( $p$ ). It should be emphasized here that this difference in the level of stress-concentration resulting from the same geometry is of crucial importance to our analysis.

Figure 2A depicts the stress field due to the application of hydrostatic pressure alone to a filled hole. (Two-dimensional elements are considered here, however, the analysis can be extended to three dimensions). When the hole is not filled with liquid, an additional stress field produced by a negative pressure of the same magnitude must be added over the boundary in order to maintain zero radial stress. This is shown in figure 2B. It is therefore obvious that a combination of the stress fields shown in 2A and 2B produces the stress field associated with an empty hole under hydrostatic pressure alone.

We are interested, however, in the application of a tensile stress field concurrently with hydrostatic pressure. Figure 2C illustrates such a tensile stress field in relation to the hole (empty or filled). The tensile component of the stress field as illustrated in figure 2C and the additional compressive stress component  $p$  of figure 2B are expected to be concentrated at the tip of the hole (shown by dark squares). The concentrated values are denoted, respectively, by  $c_1\sigma$  and  $c_2p$  where  $c_1$  and  $c_2$  are the corresponding stress concentration factors. Accordingly, the maximum normal stress at the tip of the hole filled with the pressure-transmitting fluid can be given by

$$\sigma_{\max}^f = c_1\sigma - p \quad (1)$$

On the other hand, the maximum normal stress at the tip of the empty hole can be expressed as

$$\sigma_{\max}^e = c_1\sigma - p - c_2p \quad (2)$$

Of course, this treatment assumes that the polymer-liquid chemical interaction is negligible. Such a restriction can be safely applied to pressure-transmitting fluids like silicone oil which was used in our experiments. This fluid was found to have negligible effects on the craze initiation stress of polymers under atmospheric pressure<sup>1</sup>.

Several possible routes can be pursued in an attempt to reach a viable craze initiation criterion which does not contradict the experimental results. The only criterion considered here shall be the maximum normal stress  $\sigma_{\max}$  at the tip of the most dangerous flaw. The critical value of  $\sigma_{\max}^f$  should be the same as  $\sigma_{\max}^e$  for the specific polymer-liquid system.

### 3. Experimental

Poly methylmethacrylate (PMMA) cylindrical test specimens were machined from commercial material (Cadillac Plastic and Chemical Co.). The overall specimen length was 2.40 in. with a reduced gauge length of 1.0 in. and 0.12 in. diameter. Metallographic techniques employed by Baer and coworkers<sup>1</sup> were carefully followed after which test specimens were annealed in vacuum for 50 hours at 90°C, then slowly cooled to room temperature. A detailed discussion of the tensile test procedure under high hydrostatic pressure, together with an account for the apparatus used has been given elsewhere.<sup>1</sup>

Craze initiation stress was estimated from the point of inflection on the tensile stress-strain curves obtained under hydrostatic pressures up to 100 MPa.

### 4. Results

Figure 3 shows the dependency of craze initiation stress of PMMA on the applied hydrostatic pressure for both protected and exposed samples. When the polymer was protected from the fluid environment (silicone oil, 200 cSt.) crazing was only observed up to 20 MPa, beyond this, shear yield was observed. This brittle-to-ductile transition has been previously observed by Baer and coworkers.<sup>11</sup> On the other hand, crazing was observed in samples exposed to the pressure transmitting fluid at all pressures up to 100 MPa. In both cases, the craze initiation stress was observed to be a linear function of pressure.



Figure 4 shows similar results on the pressure dependency of craze initiation in polystyrene reported recently<sup>1</sup>. Again, the craze initiation stress was found to be a linear function of pressure. For both PMMA and PS, the craze initiation of exposed specimens showed a lower pressure coefficient than specimens protected from the environmental fluid.

## 5. Discussion

The usefulness of the criterion presented above, i.e. crazing occurs when the maximum stress at the tip of the flaw reaches a critical value independent of whether or not the flaw is filled with an environmental liquid, shall be demonstrated. For PMMA, to obtain the critical value of maximum stress outlined above, the stress concentration factors  $c_1$  and  $c_2$  have to be assigned the values 2.5 and 1.2 respectively. Using these values in equations (1) and (2) predicts that craze initiation occurs at a critical maximum normal stress in the order of 125 MPa at all pressures up to 100 MPa for both exposed and protected specimens as shown in table 1. The consistency of the data in table 1 for PMMA lends support to the proposed criterion.

For PS it was found that  $c_1 = 2.7$  and  $c_2 = 1.7$  should be adopted in order to obtain the critical craze initiation stress. The calculated values of  $\sigma_{\max}$  for polystyrene as a function of pressure up to 100 MPa are shown in table 2. These values indicate that crazing would occur in polystyrene when the stress level ( $\sigma_{\max}$ ) reaches a critical value of 93 MPa for all pressures.

The stress concentration values adopted in the above treatment can readily be calculated from slightly elliptical holes with their long axes perpendicular to the direction of the applied tensile force. It is not unreasonable to assume that flaws may acquire this geometry as a structural feature of glassy polymer surfaces. Stress concentration values close to those reported here can be derived from a surface histogram

reported by Argon and Hanoosh<sup>12</sup> for polystyrene specimens metallographically treated in a similar fashion. Moreover, Gent<sup>10</sup>, in his recent analysis for the data shown in figure 4, realized that a stress concentration factor  $c_1 = 3$  was necessary to obtain agreement between his theory and this experiment.

It is readily deduced that while the remote stress field is compressive and the first stress invariant is negative at pressures close to 100 MPa, a relatively small stress concentration can produce a maximum tensile force capable of initiating crazes. The present criterion not only predicts craze initiation in compressive stress fields but also explains the observation of crazes in pure torsion where the first stress invariant is zero. This approach contrasts but does not contradict the current theories requiring a positive first stress invariant.

## 6. Conclusions

A criterion for craze initiation in glassy polymers has been presented which suggests that crazing occurs when the maximum normal stress ( $\sigma_{\max}$ ) at the tip of a flaw reaches a critical value. When a hydrostatic pressure was superposed on the applied tensile force, the craze initiation stress for PMMA and PS was found to be independent of the pressure for specimens protected from and exposed to the pressure-transmitting fluid.

Our analysis demonstrated that small stress concentrations resulting from slightly elliptical flaws - in contrast to previously conceived sharp notches - act as craze initiators even under remote macroscopic stress fields.

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### Figure captions

- Figure 1:      a) Surface Microheterogeneities acting as stress concentrators.  
                 b) filled with environmental fluid (exposed) and  
                 c) empty (protected).
- Figure 2:      Components of the stress fields considered:  
                 (A) filled hole under hydrostatic pressure only.  
                 (B) additional stress field necessary to compensate for  
                 the hydrostatic pressure (see text) and  
                 (C) remote tensile stress field.
- Figure 3:      Pressure dependency of remote craze initiation stress for  
                 PMMA protected from and exposed to the pressure-transmitting  
                 fluid.
- Figure 4:      Pressure dependency of remote craze initiation stress for  
                 PS protected and exposed to the pressure-transmitting fluid.

Table captions

Table 1: Craze initiation stress  $\sigma_{\max}$  for PMMA as a function of pressure; both protected from and exposed to pressure-transmitting fluid.

Table 2: Craze initiation stress  $\sigma_{\max}$  for PS as a function of pressure; both protected from and exposed to pressure-transmitting fluid.

Table 1

Pressure, MPa	0	10	20	30	40	60	70	80	100
$\sigma_{\max}$ , MPa (Protected)	125	123	123	BD	-	-	-	-	-
$\sigma_{\max}$ , MPa (Exposed)	125	125	123	130	127	125	123	126	130

BD = Brittle-to-Ductile Transition.

Table 2

Pressure, MPa	10	20	30	40	50	60	82	100
$\sigma_{\max}$ , MPa (Protected)	97	92	93	BD	-	-	-	-
$\sigma_{\max}$ , MPa (Exposed)	97	93	92	92	96	91	88	93

BD = Brittle-to-Ductile Transition.



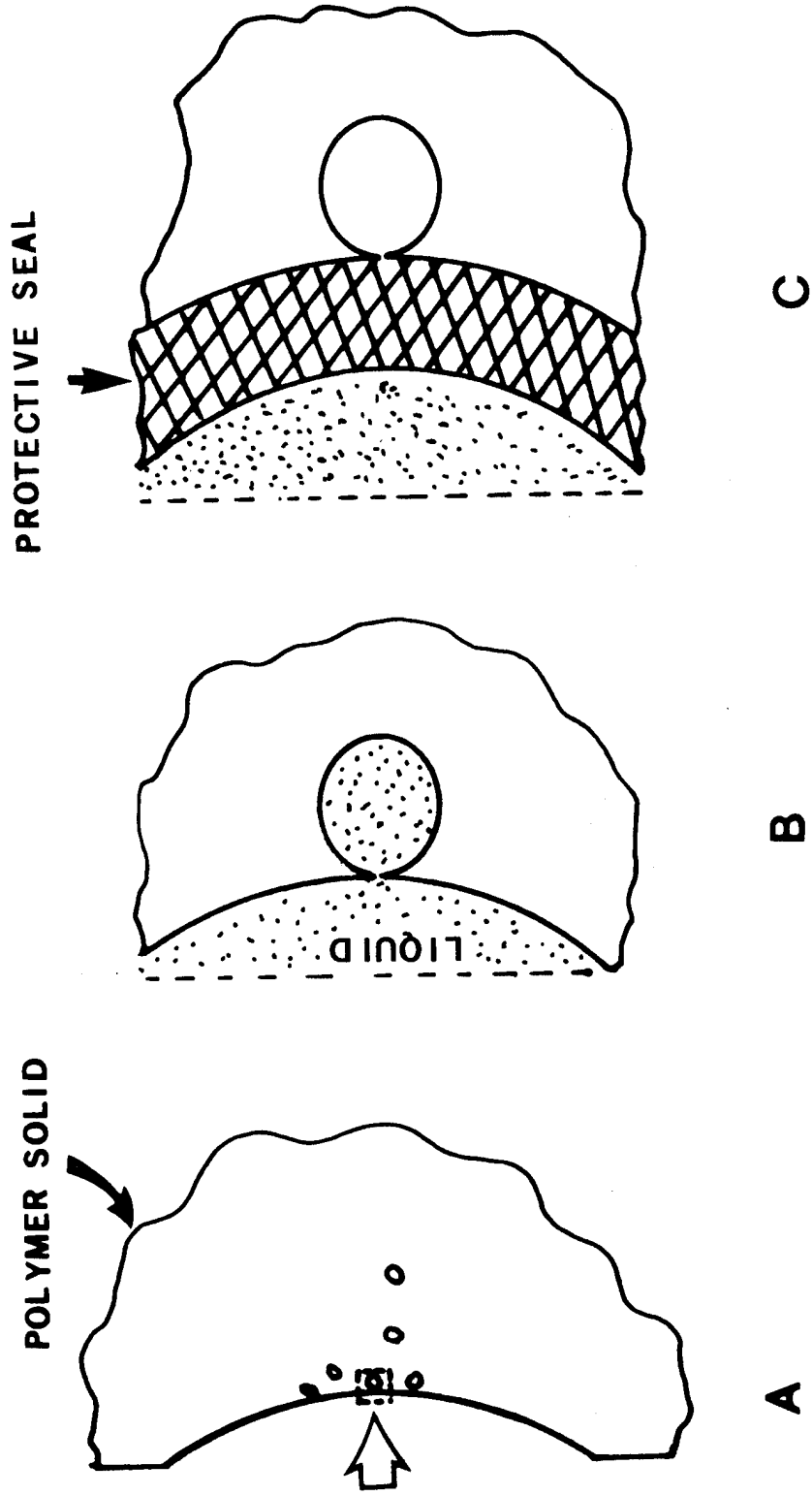
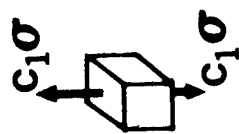
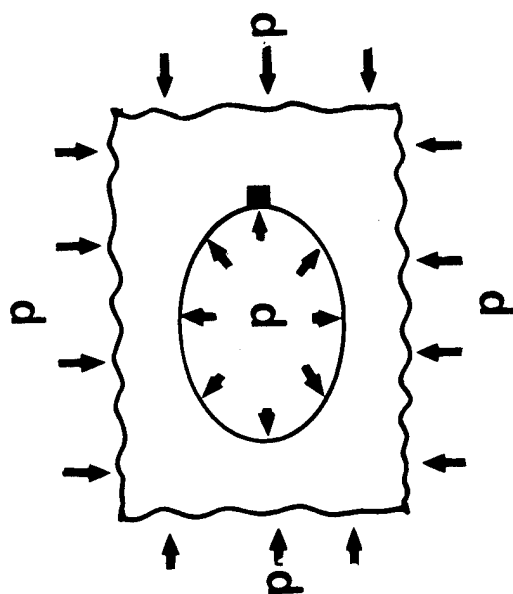
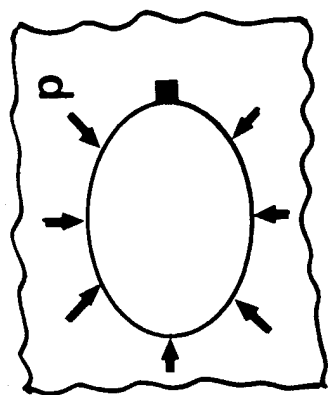
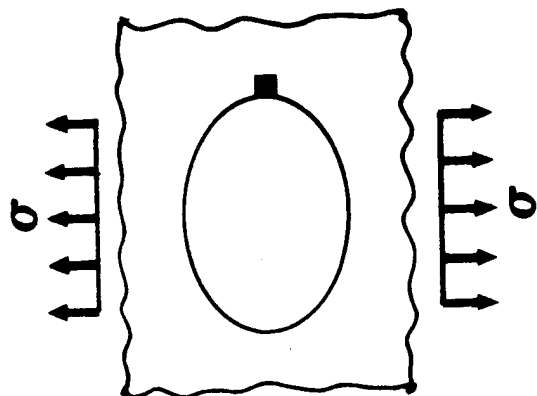
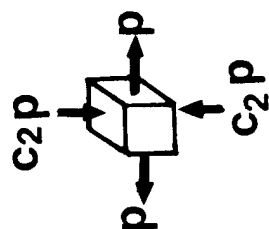


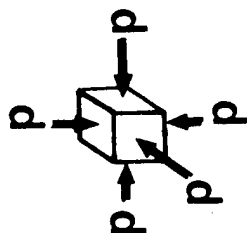
Fig. 1



C



B



A

Fig. 2

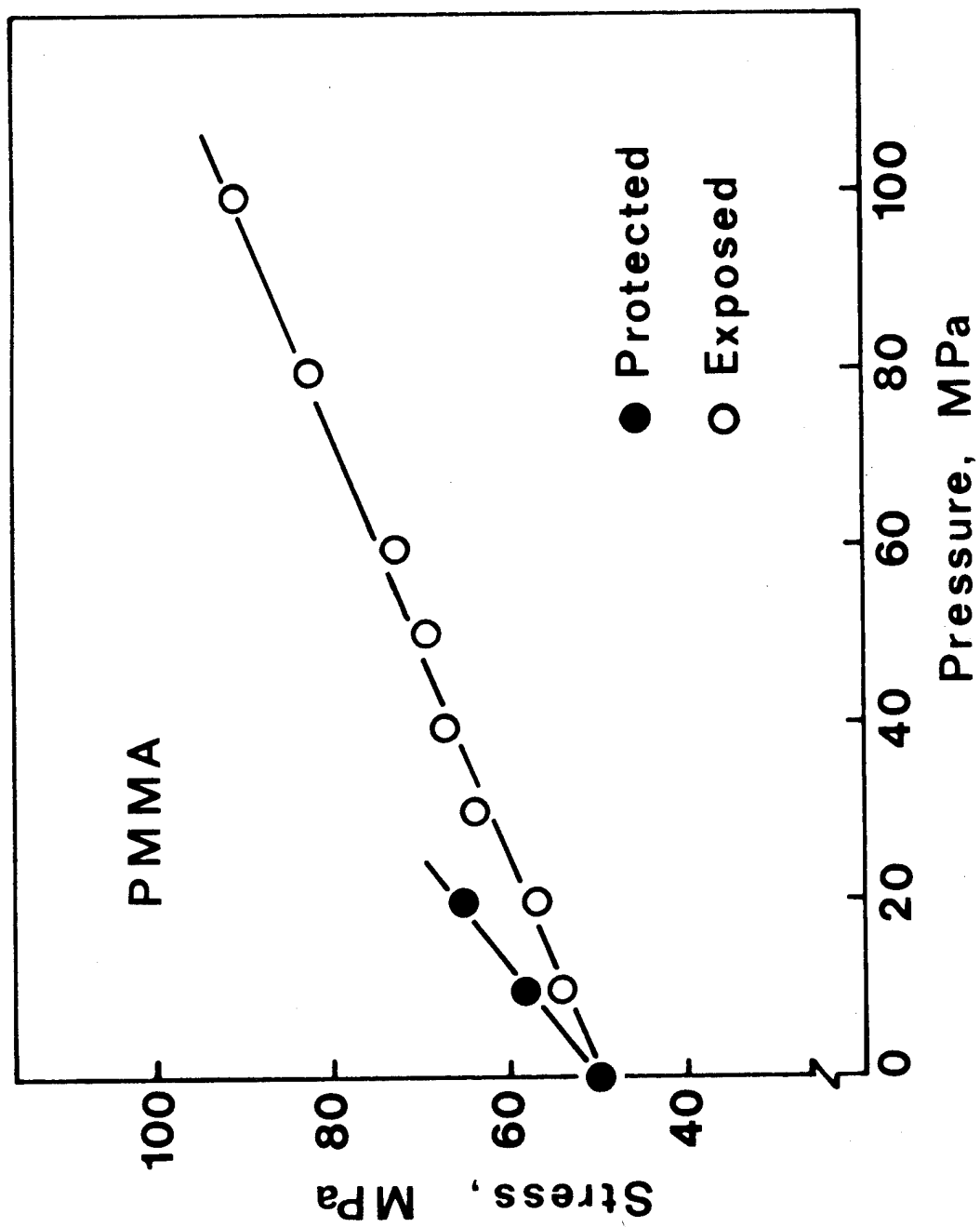


Fig. 3

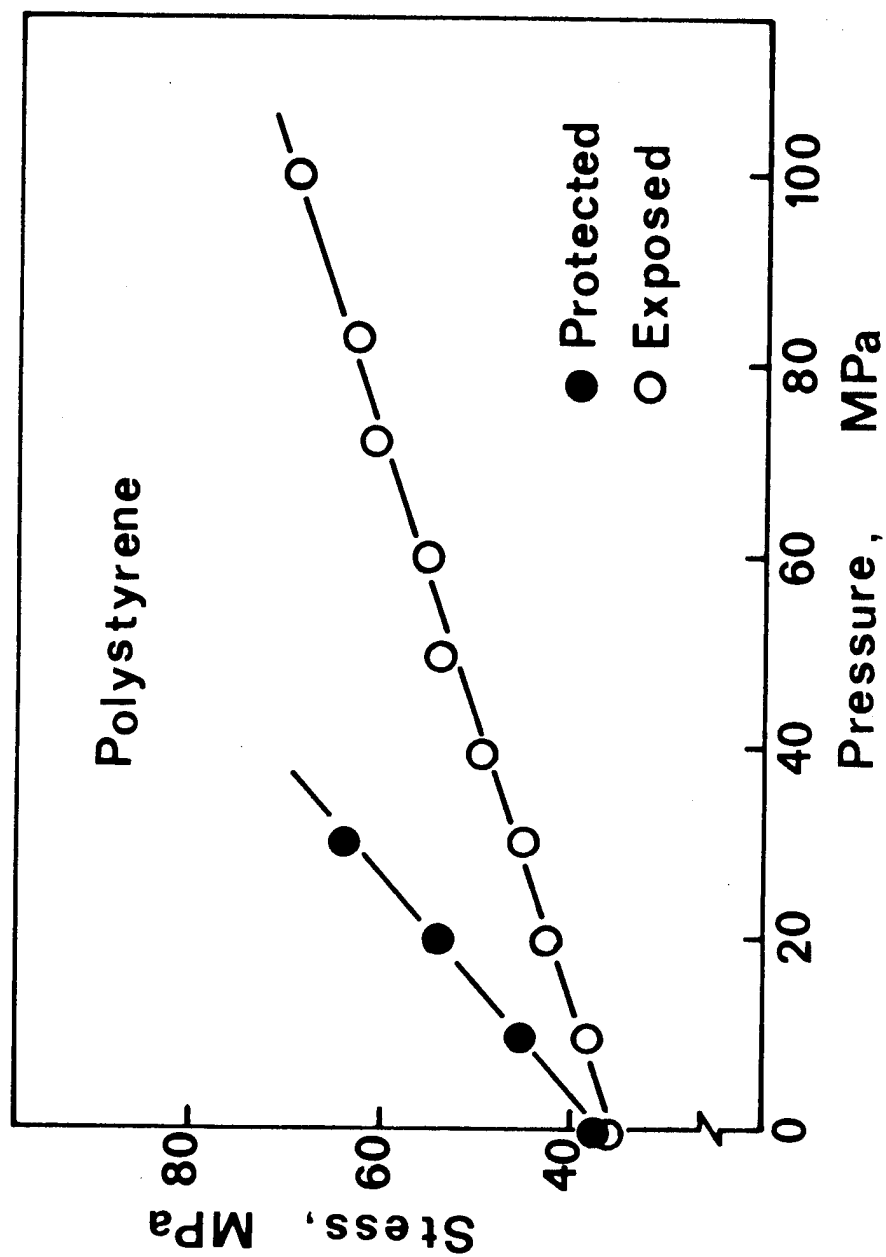


Fig. 4